A RELATIONSHIP BETWEEN PITZER'S ACENTRIC FACTOR AND THE MORSE INTERMOLECULAR POTENTIAL*

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ABSTRACT

A connection is found between Pitzer's acentric factor and the parameter c which governs the curvature of the Morse potential function at its minimum. This not only provides a physical interpretation for c, but also has practical implications which are explored briefly.

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Pitzer and coworkers[1-4] developed and applied a theory of the volumetric and thermodynamic properties of fluids involving a factor which is a measure of the acentricity of the molecule. The essential point is that nonpolar, nonquantum fluids with equal values of the acentric factor satisfy the law of corresponding states. Although it was realized that the theory might be stated in terms of a suitable three-parameter potential model,[1] the bulk of its development[2,3] was couched instead in terms of the critical temperature T_c, the critical pressure P_c, and the acentric factor ω, defined by

$$\omega = - \log (P/P_c) - 1.000 . \qquad (1)$$

Here P is the vapor pressure measured at a temperature $T = 0.7T_c$. Only recently has an explicit connection been made[4] between and a linear dimension of the core of the Kihara potential.[5]

Instead of the Kihara model, let us consider the Morse potential,

$$\varphi(r) = \epsilon \left\{ \exp \left[-2(c/\sigma)(r-r_m) \right] \quad -2 \exp \left[-(c/\sigma)(r - r_m) \right] \right\} .$$

The significance of the Morse potential parameters has been

discussed in detail elsewhere.[6] Only the relation between c and the curvature of the potential at the equilibrium separation r_m need be mentioned here:

$$(\partial^2\varphi/\partial r^2)_{r=r_m} = c^2(2\epsilon/\sigma^2) .$$

Since Pitzer[1] and Balescu[7] showed that the curvature of the potential increases with increasing acentricity of the molecule in question, it is reasonable that a relation between ω and c should exist.

From a comparison of the published values for ω^2 with the values of c suggested for N_2 and the heavy rare gases[8] and for a number of hydrocarbons,[9] it can be shown that

$$c = 5 + 11\,\omega . \qquad (2)$$

This relationship, together with Eq. (1), establishes the physical significance of the Morse parameter c. The additive constant is fixed by the condition that $\omega \approx 0$ for the rare gases[1,2] together with the observation that $c \approx 5$ for these simple fluids.[8] Recently a set of empirical rules have been developed in order to estimate the Morse parameters for the n-alkanes.[9] For c, the rule is:

$$c = 5 + 0.55\,n ,$$

where n is the number of carbon atoms in the n-alkane. This equation together with the approximation

$$\omega \approx 0.05\ n \quad ,$$

which is valid for most n-alkanes except methane,[2] then fixes the second constant in Eq. (2).

In Table I values of c obtained from published values of ω^2 via Eq. (2) are compared with the "most likely" values.[8,9] The latter are obtained by fitting experimental second virial coefficients and viscosities. The agreement between the two sets of c values is rather good.

These results, together with those of Danon and Pitzer[4], suggest that the acentric factor provides a simple and reliable method for determining what is effectively the "well-width" parameter for certain three-parameter potentials. As a practical consequence, the task of assigning the parameters of the Kihara or the Morse potential becomes no more difficult than that for the Lennard-Jones(12-6) potential. Once all the parameters of such potentials are fixed, calculations of a host of macroscopic properties are again just as easy to perform as with the (12-6) potential. From these practical considerations, then, there seems to be no real advantage in using the "simpler" (12-6) potential instead of the "more complicated"

Kihara or Morse potentials.

So far, an explicit connection between the acentric factor and an intermolecular potential has been accomplished only for the Kihara and Morse models. There is no a priori reason to believe that such a relation should not be established for any sufficiently realistic potential model.

TABLE I

A Comparison of the "most likely" values of the Morse parameter c with those calculated from the acentric factor.

Substance	Calculated, Eq. (2) [a]	"Most likely" [b]
Ar	4.978	5.064
Kr	4.978	4.905
Xe	5.022	4.989
N_2	5.440	5.238, (5.482)
methane	5.143	5.561
ethane	6.155	6.096
propane	6.672	6.313
n-butane	7.211	7.751
n-pentane	7.772	7.681
n-heptane	8.872	9.070
n-octane	(9.400)	9.612
benzene	7.365	6.519, (7.164)

a Values of ω taken from Ref. 2 . The ω for n-octane was obtained by linear extrapolation.

b Taken from "most likely" potentials reported in Ref. 9 for the hydrocarbons and in Ref. 8 for the remaining substances. The values in parentheses correspond to the E_3 potentials discussed in those references. Insofar as they agree better with the values obtained from the acentric factor, they may be the more realistic potentials.

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